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【List of the Annexed Documents】

【Document】 Specification One copy

【Document】 Abstract One copy

【Proof】 Requested

【Document】 SPECIFICATION

【Title of the Invention】 PHOTOSENSITIVE RESIN LAMINATE AND PLATE FOR SIGNBOARD MADE THEREOF

【What is Claimed is】

【Claim 1】 A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin laminate shows a total light transmission of not less than 60%.

【Claim 2】 A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, which laminate satisfying the following formula (1):

$$\frac{(A-B)}{A} \times 100 \leq 15 \quad (1)$$

wherein A is a total light transmission (%) of the support and B is a total light transmission (%) of the photosensitive resin laminate.

【Claim 3】 The photosensitive resin laminate of claim 1 or claim 2, wherein the photosensitive resin layer has a thickness of not less than 500 μm, and a Shore hardness of not less than 50.

【Claim 4】 A plate for a signboard comprising the photosensitive resin laminate of any of claims 1 to 3.

【Detailed Description of the Invention】

【Technical Field to which the Invention Pertains】

The present invention relates to a photosensitive resin laminate and a plate for a signboard made thereof, which are used for signboards such as display panel, decoration shield, name plate, Braille board and the like. Particularly, the present invention provides a signboard superior in design.

【Prior Art】

A photosensitive resin layer exposed to light through a pattern and thereafter developed to produce a photosensitive resin laminate for signboard is disclosed in JP-A-58-55927,

JP-A-9-6267 and the like and used for display panels having a relief, signboards containing Braille and the like.

However, there is a demand in the market with regard to signboards in these days for bending processing during processing of signboards, producing transparent signboards and the like. However, a photosensitive resin laminate for general use, which comprises a phenol board as a support, is not suitable for bending during processing of a signboard or production of a transparent signboard. Even when a transparent and colorless substrate is used as a support, the photosensitive resin itself is colored. Accordingly, there has arisen a demand on a photosensitive resin laminate suitable for processing into a signboard having a good design.

A photosensitive resin composition contains a naphthoquinone compound and the like for the purpose of inhibiting thermal polymerization and for adjusting sensitivity and the like. Because of the color of these compounds themselves, production by a composition containing these compounds inevitably results in a colored photosensitive resin, which is problematic for use as a signboard having a superior design. Even if the amount of addition of these compounds is reduced with the hope of suppressing the coloring, the polymer becomes a gel during the production, thus practically preventing the production.

【Problems to be Solved by the Invention】

It is therefore an object of the present invention to obtain a photosensitive resin laminate for signboards usable for display panel, decoration shield, name plate, Braille board and the like, which laminate has a superior design, which can be bent during processing of a signboard, and from which a transparent signboard can be produced.

【Means of Solving the Problems】

The present inventors have conducted intensive studies in an attempt to solve the above-mentioned problems and completed

the present invention. That is, the present invention provides

(1) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin laminate shows a total light transmission of not less than 60%.

(2) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, which laminate satisfying the following formula (1), wherein A is a total light transmission (%) of the support and B is a total light transmission (%) of the photosensitive resin laminate.

(3) The photosensitive resin laminate of the above-mentioned (1) or (2), wherein the photosensitive resin layer has a thickness of not less than 500 μm and a Shore hardness of not less than 50.

(4) A plate for a signboard comprising the photosensitive resin laminate of any of the above-mentioned (1) to (3).

$$\frac{(A-B)}{A} \times 100 \leq 15 \quad (1)$$

【Embodiment of the Invention】

The present invention is now explained in more detail.

The characteristic of the present invention is that the photosensitive resin laminate as a whole has a total light transmission of not less than 60%. The photosensitive resin layer to be used in the present invention preferably has a total light transmission of not less than 60%, more preferably not less than 70%, and particularly preferably not less than 75%. The photosensitive resin composition to be used as the photosensitive resin layer may be known, and is exemplified by a soluble polymer compound (e.g., poly(vinyl alcohol), polyamide, polyether ester amide, polyether amide, polyurethane and the like), photopolymerizable or

photocrosslinkable monomer (e.g., acrylate of polyhydric alcohol, epoxy acrylate of polyhydric alcohol, N-methylolacrylamide and the like), photopolymerization initiator (e.g., benzyldimethyl ketal, benzoindimethyl ether and the like), and a photosensitive resin composition containing, where necessary, a plasticizer, a surfactant, a dye and the like.

As the additives that can be used in the present invention, additives such as heat stabilizers including phenothiazine and hydroxylamine derivative, such as cupferron derivative, and the like can be mentioned. Referring to the mixing ratio of these, when the resin solid is less than 0.005 wt%, the thermal polymerization inhibitory effect is not exerted, causing polymer gelation at halfway during the production, whereas when it exceeds 0.05 wt%, the resin produced becomes colored, thereby giving rise to a difficulty in producing a transparent resin. Thus, to make the photosensitive resin layer transparent and colorless, the mixing ratio is preferably 0.005 - 0.05 wt%, more preferably 0.01 - 0.03 wt%.

Furthermore, hydroquinone, hydroquinone monomethyl ether, 2,6-di-t-butyl-p-cresol and the like may be added in a proportion of 0.001 - 5 wt% as a polymerization inhibitor. It is also possible to alter the properties of a photocured substance by adding a plasticizer, such as low molecular weight plasticizers (e.g., ester, amide and the like), and oligomers (e.g., polyester, polyether, liquid rubber and the like).

The aforementioned photosensitive resin layer preferably has a thickness of not less than 500 μm, particularly 800 - 1200 μm. The Shore hardness is preferably not less than 50, particularly preferably 55 - 65.

The support (hereinafter sometimes to be referred to as a supporting plate) to be used in the present invention

preferably has a total light transmission of not less than 60%, more preferably not less than 70% and particularly preferably not less than 80%. Examples thereof include glass plate, colorless polymer-molded plate such as polyethylene terephthalate resin and acrylic resin and the like. The resin of this polymer-molded plate may be made of a resin modified by copolymerization or blending or a resin modified by adding an additive such as a plasticizer and the like. The support has a thickness of not less than 1 mm and a thickness generally in the range of 1 mm - 10 mm is employed depending on the use and design. When the support has a thickness of less than 1 mm, the support itself may warp easily, which is not suitable for signboard use, whereas a thickness exceeding 10 mm is unpreferable because the plate does not cut easily and inconveniently weighs too much.

For production of the photosensitive resin laminate of the present invention, an adhesive to be mentioned later is applied on the aforementioned supporting plate and a photosensitive resin layer is laminated, which can be performed by a known method. For example, an optional method, such as heat press, injection molding, melt extrusion, solution casting, lamination and the like, can be employed to perform lamination on the aforementioned support.

The aforementioned photosensitive resin layer may be laminated in advance on, for example, a resin film of polyethylene terephthalate and the like as a support (hereinafter to be referred to as a photosensitive resin laminate precursor) and, when preparing a signboard therefrom, it is laminated on the aforementioned supporting plate having a thickness of not less than 1 mm upon peeling off of the resin film.

The aforementioned photosensitive resin laminate precursor can be prepared by a method generally employed for forming a photosensitive resin laminate for a printing plate.

For example, a photosensitive resin composition is melt-extruded in between the aforementioned resin film (preferably without an adhesive in this case) and a 125 μm-thick polyester cover film having a layer of non-adhesive transparent polymer that can be dispersed or dissolved in a developing solution [(poly(vinyl alcohol), celluloses and the like, which is also called a slip coat layer)] in a thickness of 1 - 3 μm, whereby a photosensitive resin laminate precursor comprising a resin film, a photosensitive resin layer, a slip coat layer and a cover film in this order from the bottom can be obtained.

In the present invention, the adhesive layer used for adhering a photosensitive resin layer (optionally having a slip coat layer and a cover film) to the aforementioned supporting plate may be a known adhesive. Examples thereof include polyester urethane adhesives wherein a soluble polyester is cured with polyhydric isocyanate, epoxy adhesives and the like. Of these, polyester urethane adhesive is preferable because it is superior in the adhesion to polyethylene terephthalate resin and modified polyethylene terephthalate resin. The adhesive layer composition may contain small amounts of other components. Examples of the additive include plasticizer, dye, ultraviolet absorber, halation preventive, surfactant, photopolymerizable vinyl monomer and the like.

An adhesive layer is formed on a support typically by applying a solution of the composition for adhesive layer in a predetermined thickness and removing the solvent. The application method may be known, such as roll coater, curtain flow coater, slit die coater, gravure coater, spray and the like. The adhesive layer after coating on a support is generally dried by blowing hot air in a drying furnace. The adhesive layer of the present invention may be dried at not less than 30°C and not more than 120°C for a suitable period of time, but a temprerature of not more than 70 °C is preferable

in view of thermal deformation of the support. The treatment for 1 min - 30 min is appropriate.

The adhesive layer preferably has a thickness of 0.5 μ - 100 μ. When the thickness is not more than 0.5 μ, the adhesive power is difficult to achieve between the photosensitive resin layer and the adhesive layer, whereas when it exceeds 100 μ, a problem of entrained bubbles occurs due to foaming during drying of the liquid applied. In view of the above, the adhesive layer preferably has a thickness of 0.5 μ - 100 μ, particularly preferably 1 μ - 50 μ.

The photosensitive resin laminate of the present invention comprising a supporting plate, an adhesive layer and a photosensitive resin layer, which may further have a slip coat layer and a cover film, has a total light transmission of not less than 60%, preferably not less than 70%, particularly preferably not less than 75%. When the total light transmission is less than 60%, the photosensitive resin laminate may be colored or opacified, making the appearance poor, and color tone may vary during post-processing, such as painting and the like, which is unpreferable.

When A is a total light transmission (%) of the support and B is a total light transmission (%) of the photosensitive resin laminate, it is preferable to satisfy the aforementioned formula (1). In the formula (1), the value on the right side of the equation is desirably not more than 10, particularly not more than 5. When the aforementioned formula (1) is not met, the photosensitive resin laminate has poor appearance due to coloring and turbidness, which is unpreferable because it causes different color tone during the post-processing such as painting and the like.

A signboard can be prepared from the photosensitive resin laminate of the present invention according to a method generally used for producing printing plates. For example, a negative film or positive film having a transparent image part

is closely adhered onto a photosensitive resin layer via a slip coat layer or otherwise, and an actinic ray is shot thereon to insolubilize and cure only the exposed part. The actinic radiation is obtained from a light source generally having a wavelength of 300 - 450 nm, such as high pressure mercury lamp, ultrahigh pressure mercury lamp, metal halide lamp, xenon lamp, chemical lamp and the like.

Then, an unexposed part is removed by dissolution in a suitable solvent, particularly neutral water in the present invention, whereby a relief plate having a clear image part is obtained. For this end, spray developing apparatus, brush developing apparatus and the like can be used.

Following the above methods, a signboard having a relief can be produced. Various signboards can be obtained, which expands the range of use, by applying a paint containing colorant, ultraviolet absorber and the like to the relief, putting gold leaf on letters and images, applying a paint, drawing a pattern on the back of the support or coloring the support, adhering a decorative laminate sheet and the like, or where necessary, bending while heating the support and the like.

[Examples]

The present invention is explained in detail by referring to examples. The present invention is not limited by these examples in any way. The total light transmissions in Examples were measured using a turbidimeter (haze meter, NDH-1001DP Nippon Denshoku Industries Co., Ltd.).

Reference Example 1

As the photosensitive resin composition to be laminated, ε-caprolactam (525 parts), nylon salt (400 parts) of N-(2-aminoethyl)piperazine and adipic acid, and nylon salt (75 parts) of 1,3-bis(aminomethyl)cyclohexane and adipic acid were subjected to melt condensation polymerization in an autoclave to give a nylon copolymer. The obtained polymer (55 parts), N-

nitrosophenylhydroxylamine aluminum salt (0.01 part), hydroquinone monoethyl ether (0.1 part) and N-ethyltoluenesulfonamide (7 parts) were dissolved in a mixed solvent of methanol (47 parts) and water (96 parts) at 60°C, and glycidyl methacrylate (2 parts) was added. The mixture was stirred for 2 h to allow reaction of glycidyl methacrylate with the polymer terminal. To this solution were added ammonium sulfite (0.3 part), oxalic acid (0.3 part) and methacrylic acid (4 parts), after which acrylate (31 parts) obtained by opening addition reaction of triglycidyl ether of trimethylolpropane and acrylic acid, and benzyl dimethyl ketal (1.0 part) were added to give a solution of a photosensitive resin composition. This solution was cast on a polyester film and methanol was evaporated to give a photosensitive resin composition **a** having a thickness of about 800 μm.

Reference Example 2

In the same manner as in Reference Example 1 except that phenothiazine (0.04 part) was added instead of N-nitrosophenylhydroxylamine aluminum salt (0.01 part), a photosensitive resin composition **b** was obtained.

Reference Example 3

In the same manner as in Reference Example 1, copolymerized nylon polymer (55 parts), N-nitrosophenylhydroxylamine aluminum salt (0.01 part), hydroquinone monoethyl ether (0.1 part), and N-ethyltoluenesulfonamide (7 parts) were dissolved in a mixed solvent of methanol (47 parts) and water (96 parts) at 60°C, and glycidyl methacrylate (2 parts) was added. The mixture was stirred for 2 h to allow reaction of glycidyl methacrylate with the polymer terminal. To this solution were added ammonium sulfite (0.3 part), oxalic acid (0.3 part) and methacrylic acid (4 parts), after which acrylate (31 parts) obtained by opening addition reaction of triglycidyl ether of trimethylolpropane and acrylic acid, benzyl dimethyl ketal

(1.0 part) and phenothiazine (0.02 part) were added to give a solution of a photosensitive resin composition. This solution was cast on a polyester film and methanol was evaporated to give a photosensitive resin composition **c** having a thickness of about 800 μm.

Reference Example 4

In the same manner as in Reference Example 1 except that 1,4-naphthoquinone (0.04 part) was added instead of N-nitrosophenylhydroxylamine aluminum salt (0.01 part), a photosensitive resin composition **d** was obtained.

Reference Examples 5 - 7 (preparation of support)

As a support, 2 mm-thick acrylic resin (ACRYLITE manufactured by MITSUBISHI RAYON), hard vinyl chloride resin (vinyl chloride board manufactured by MEIVAN,) and modified polyethylene terephthalate resin (SUNDAY PET manufactured by ACRYSUNDAY Co., Ltd.) having a total light transmission shown in the following Table 1 were used.

As an adhesive layer, used was a polyester urethane adhesive, and a solution of the composition for adhesive layer was prepared as follows. A polyester resin (VYLON RV-200, 80 parts by weight, Toyo Boseki Kabushiki Kaisha) was heated and dissolved in a mixed solvent (1940 parts by weight) of toluene/methyl ethyl ketone=80/20 (weight ratio) at 80°C. After cooling, DESMODUER HL (20 parts by weight, Sumitomo Bayer Urethane) obtained from hexamethylene diisocyanate and toluene diisocyanate was used as an isocyanurate type polyhydric isocyanate, and triethylenediamine (0.06 part by weight) was added as a curing catalyst, after which the mixture was stirred for 10 min.

The thus-obtained solution of the composition for adhesive layer was applied on the aforementioned respective supports each having a thickness of 2 mm, such that a film thickness was 7 μm, cure-dried at 50°C for 15 min to give a support (hereinafter to be referred to as acrylic plate, vinyl

chloride plate and PET-G) having an adhesive layer.

Table 1

		total light transmission A (%)
support	acrylic plate	92.8
	vinyl chloride plate	79.3
	PET-G	89.8

Examples 1 - 3

The photosensitive resin composition **a** obtained in Reference Example 1 and the support obtained in Reference Examples 5 - 7, which had an adhesive layer, were adhered and water was poured therebetween. A photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap clearance had been adjusted according to the thickness of the laminate, to give a transparent and colorless photosensitive resin laminate. The results are shown in Table 2.

Examples 4 - 6

The photosensitive resin composition **b** obtained in Reference Example 2 and the support obtained in Reference Examples 5 - 7, which had an adhesive layer, were adhered and water was poured therebetween. A photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap clearance had been adjusted according to the thickness of the laminate, to give a transparent and colorless photosensitive resin laminate. The results are shown in Table 2.

Examples 7 - 9

The photosensitive resin composition **c** obtained in Reference Example 3 and the support obtained in Reference Examples 5 - 7, which had an adhesive layer, were adhered and

water was poured therebetween. A photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap clearance had been adjusted according to the thickness of the laminate, to give a transparent and colorless photosensitive resin laminate. The results are shown in Table 2.

Comparative Examples 1 - 3

The photosensitive resin composition **d** obtained in Reference Example 4 and the support obtained in Reference Examples 5 - 7, which had an adhesive layer, were adhered and water was poured therebetween. A photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap clearance had been adjusted according to the thickness of the laminate, to give a transparent and colorless photosensitive resin laminate. The results are shown in Table 3.

Table 2

	photosensitive resin composition	support	total light transmission of laminate	((A-B)/A) ×100
Example 1	**a**	acrylic plate	88.4	4.7
Example 2	**a**	vinyl chloride plate	71.2	10.2
Example 3	**a**	PET-G	80.5	10.4
Example 4	**b**	acrylic plate	84.9	8.5
Example 5	**b**	vinyl chloride plate	73.3	7.6
Example 6	**b**	PET-G	85.9	4.3
Example 7	**c**	Acrylic plate	85	8.4
Example 8	**c**	vinyl chloride plate	73.2	7.7
Example 9	**c**	PET-G	80.8	10

Table 3

	Comparative Example 1	Comparative Example 2	Comparative Example 3
photosensitive resin composition	**d**	**d**	**d**
support	acrylic plate	vinyl chloride plate	PET-G
total light transmission of laminate	59.8	53.3	58.5
((A-B)/A)×100	35.6	32.8	34.9

Reference Example 8

The photosensitive resin laminates of the present invention obtained in the above-mentioned Examples 1 - 9 were preserved for not less than 7 days, and a polyester film of 125 μm was peeled off, and they were exposed to light from a chemical lamp for 3 min in vacuo. Using a brush washer (100 μmϕ nylon brush, NIHON DENSHI SEIKI CO. LTD., JW-A2-PD type)

and tap water as a developing solution, the negatives were developed at 23°C for 2 min to give a signboard having a relief image.

【Effect of the Invention】

The photosensitive resin laminate for signboards of the present invention having the above-mentioned constitution has a support that can be bent easily, is characterized by the thickness of the support and transparent and colorless property, which is superior in design, and which enables provision of a photosensitive resin laminate suitable for a signboard, thus greatly contributing to the industry.

【Document】 Abstract

【Summary】

【Problems】 Provision of a photosensitive resin laminate, which is used for signboards such as display panel, decoration shield, name plate, Braille board and the like, and particularly superior in design.

【Solving Means】 (1) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin laminate shows a total light transmission of not less than 60%. (2) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, which laminate satisfying the following formula (1), wherein A is a total light transmission (%) of the support and B is a total light transmission (%) of the photosensitive resin laminate. (3) The photosensitive resin laminate of the above-mentioned (1) or (2), wherein the photosensitive resin layer has a thickness of not less than 500 μm and a Shore hardness of not less than 50. (4) A plate for a signboard comprising the photosensitive resin laminate of any of the above-mentioned (1) to (3).

$$\frac{(A-B)}{A} \times 100 \leq 15 \quad (1)$$

【Main Drawing】 None